

## MEASUREMENT OF SOFT X-RAY ABSORPTION SPECTRA WITH A FLUORESCENT ION CHAMBER DETECTOR

F.W. LYTLE and R.B. GREGOR

*The Boeing Company, Seattle, WA 98124, USA*

D.R. SANDSTROM and E.C. MARQUES

*Washington State University, Pullman, WA 99164, USA*

Joe WONG and C.L. SPIRO

*General Electric Corporate Research and Development, Schenectady, NY 12301, USA*

G.P. HUFFMAN and F.E. HUGGINS

*US Steel Corporation, Monroeville, PA 15146, USA*

Received 19 December 1983 and in revised form 29 February 1984

The problem of absorption of soft X-rays by thick Be windows in hard X-ray beam lines is well known. Although the signal at 2.4 keV was reduced by  $\sim 10^3$  we have routinely measured the absorption spectra of S (2472 eV) and elements at higher energies including Cl, Ar and K. These spectra were obtained on hard X-ray beam lines at Stanford Synchrotron Radiation Laboratory (SSRL) with Si(111) monochromator crystals and a fluorescent ion chamber detector [1]. Higher energy harmonics were minimized by detuning and the end station was enclosed in a helium bag to prevent absorption by air. Although the diminished X-ray flux and decreasing fluorescent yield were serious negative factors at these low X-ray energies the spectra from thick samples were of excellent quality with sufficient sensitivity to characterize 1% S in coal. Representative spectra are shown comparing data from focused and unfocused beam lines and with S data from JUMBO [2]. Comparison of Ar and KCl data to excellent data found in the older literature [3-5] allow a confirmation of the resolution function (energy bandpass) of the monochromator. A simple new beam line is suggested which would allow a substantial increase in low energy X-ray flux (measurements down to Al and Si) with the sample and detector in a He atmosphere.

### 1. Introduction

On hard X-ray beam lines at synchrotron radiation sources thick Be windows are used in order to secure the vacuum requirements of the storage ring. Additional absorbers in the beam may be 25  $\mu\text{m}$  of pyrolytic carbon (to absorb heat) and a Kapton window after the X-ray monochromator. All of these absorb soft X-rays with a sharp cut-off between 2 and 4 keV. Fig. 1 illustrates the case of typical beam lines at Stanford Synchrotron Radiation Laboratory (SSRL). Curve B illustrates the case for a wiggler side-station (beam lines IV-1, IV-3 and VII-3) with 533  $\mu\text{m}$  Be, 35  $\mu\text{m}$  C and 1 m He along the beam path. Curve C illustrates the effect of an additional 9 m of He which is typical of beam lines I-5, II-2 and II-3. This 9 m of He decreases flux by factors of 2-3 at the lower energies. Curve A is a hypothetical case with 125  $\mu\text{m}$  Be and 25  $\mu\text{m}$  C which will be discussed later.

Although the transmitted intensity is falling very rapidly and is down by  $\sim 10^3$  at the energy of the S K-edge. [The energies of the S (2472 eV) and K (3607 eV) edges are indicated on the graph.] We were able to obtain good data for S, Cl [6] and the higher Z elements on these beam lines. These elements also may be examined on JUMBO [2]; however, it is a particular advantage to be able to use more available beam lines and not be bothered by the high vacuum requirements of JUMBO. Herein we discuss our experimental technique, the X-ray detector, a variety of data for S, Cl, Ar and K and make comparisons between data from beam lines at SSRL and with data in the literature.

### 2. Experimental technique

We used the standard two-crystal monochromator (Super Monochromator) at SSRL with Si(111) crystals,

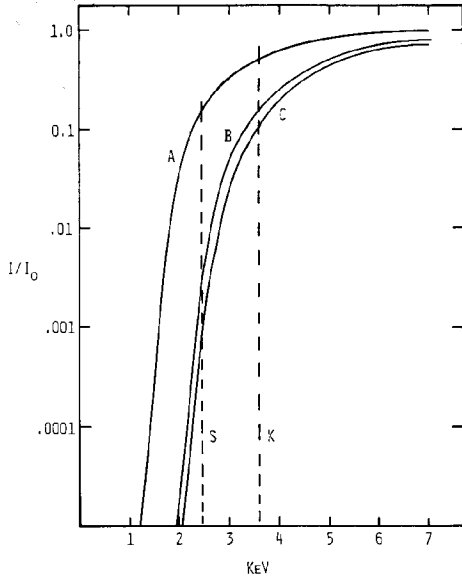


Fig. 1. Spectra calculated for (A) 125  $\mu\text{m}$  Be and 25  $\mu\text{m}$  C, (B) 533  $\mu\text{m}$  Be 35  $\mu\text{m}$  C and 1 m He (this is typical of SSRL wiggler beam lines), and (C) 533  $\mu\text{m}$  Be, 35  $\mu\text{m}$  C plus 9 m of He (SSRL beam lines I-5, II-2 and II-3).

a 1 mm (vertical dimension) entrance slit and a He path enclosing the end of the beam pipe, scatter slits,  $I_0$  detector (standard 15 cm parallel plate ion chamber) and the sample area. Windows on the  $I_0$  detector were replaced with 6  $\mu\text{m}$  polypropylene [7]. The fluorescent X-ray ion chamber detector is shown in fig. 2. This unit is derived from that described by Stern and Heald [1]. The sample is located at  $45^\circ$  to the X-ray beam. Fluorescent and scattered X-rays emerging from the surface of the sample impinge upon a filter (typically a  $Z - 1$  filter) which removes the scattered radiation and passes the fluorescent X-rays from the sample. The slit assembly is oriented as shown so that radiation diverging from the sample position passes through the slits unimpeded. The purpose of the slits is to (partially) reject the fluorescence arising in the filter material by restricting the angular aperture for this radiation. It was reported [1] that the slits reduced the fluorescence from the filter by a factor of 8. The outer window of the ion chamber is 6  $\mu\text{m}$  aluminized Mylar with a center electrode and back plane of 90% transparent Ni mesh. The outer electrodes are operated at  $-45$  V and the photoelectron current collected on the center electrode and amplified to a positive dc voltage typically between 0.1–1.0 V. This is connected to an analog-to-digital

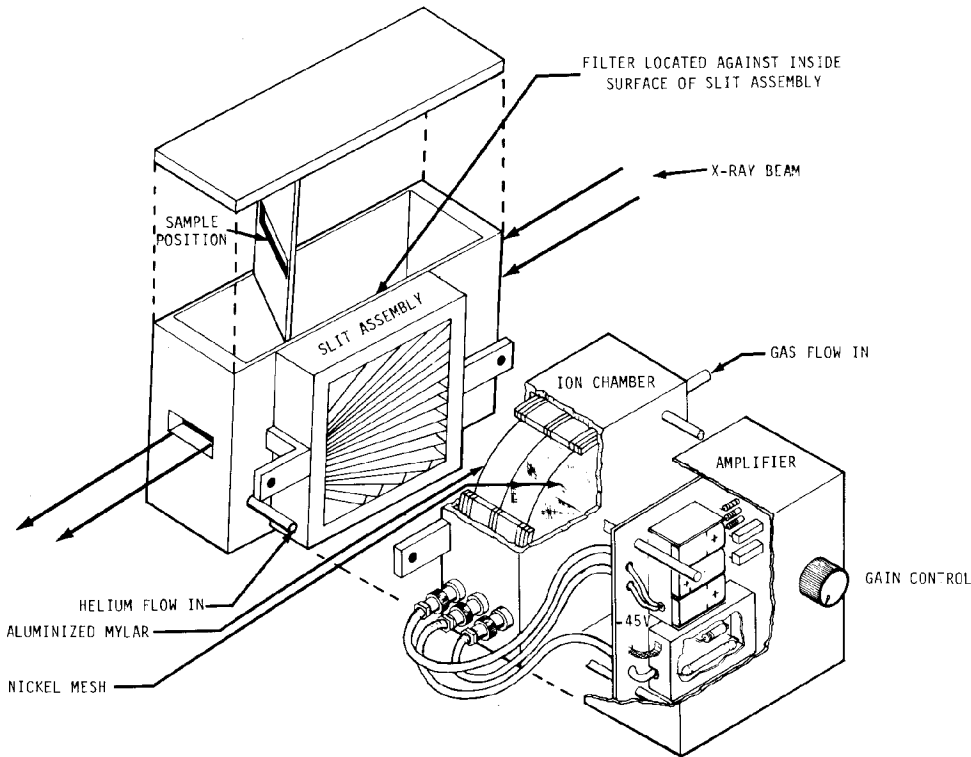


Fig. 2. Fluorescent X-ray ion chamber.

converter and scaled in the same way as the  $I_0$  detector. The active diameter of the ion chamber is 8.25 cm with a mid-sample to ion chamber distance of  $\sim 5.5$  cm. This results in a collection efficiency of  $\sim 20\%$  of  $2\pi$  from the front face of the sample.

Depending upon the element of interest various gases (or mixtures) may be used in the ion chamber. The collecting electrode is centered 1.5 cm from the aluminized Mylar front window and Ni mesh back plane. The maximum signal will be detected if the X-rays can be mostly absorbed within the body of the ion chamber, i.e., with a mean free path for absorption of 1–2 cm. Table 1 lists the calculated properties of various ion chamber gases. For S, Cl and Ar spectra nitrogen was used in the fluorescent detector; for K spectra an available mixture of 10% He, 90% Ne was used. In all cases He was used in the  $I_0$  detector. The powdered samples and NaCl solution were contained in 6  $\mu\text{m}$  polypropylene bags [7]. For the Ar experiment a small amount of Ar was mixed with the He purging the sample box. No scattered radiation filter was used for any of the measurements. For elements with  $Z < 23$  (V) the  $Z - 1$  rule no longer holds, i.e., the  $Z - 1$  absorption edge does not fall in the energy range between the  $K_\alpha$  lines and K-absorption edge of element Z. In some cases it may be possible to use elements with suitable L-edges as filters for low Z elements (e.g., I L<sub>III</sub> for Ti K-edge).

Although the (222) reflection is forbidden from Si(111) the fully tuned beam from the monochromator was primarily composed of higher harmonics. In order to even observe an absorption edge it was absolutely essential to remove the harmonics from the beam. This was conveniently done by detuning [8] the monochromator so that the diffracting planes of the two crystals were not precisely parallel. This procedure selectively removes higher order reflections [8]. Fig. 3 illustrates the detuning procedure for S. The monochromator was adjusted to an (indicated) energy position *below* the S

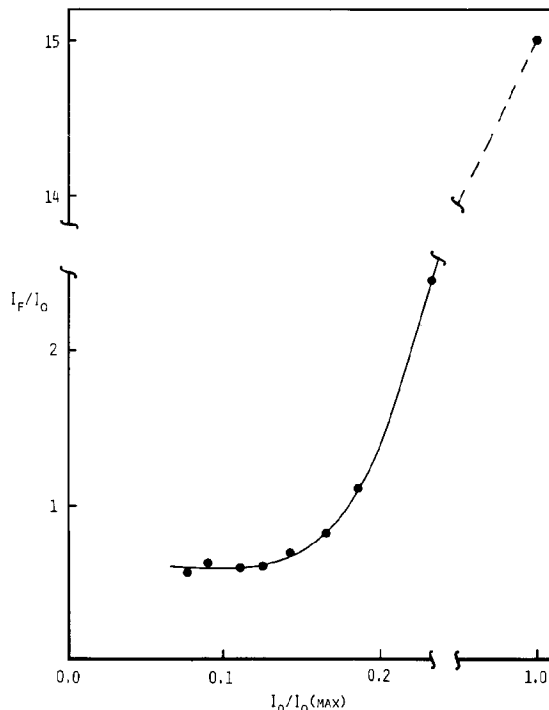


Fig. 3. The effect of detuning on intensity. The text describes the procedure.

edge. At this position only the harmonic contaminants in the beam have sufficient energy to excite K-edge fluorescent X-rays from S. When the normalized signal from the fluorescent ion chamber,  $I_F/I_0$  is plotted versus degree of detuning,  $I_0/I_0(\text{max})$ , where  $I_0(\text{max})$  is the highest observed signal from the  $I_0$  detector, the curve decreases asymptotically to a horizontal line at  $\sim 80$ – $90\%$  detuning (lesser detuning for higher energies). At this point the beam has negligible harmonic content;

Table 1  
Properties of gases for X-ray detector, calculated mean free path ( $I/I_0 = 1/e$ ), cm

Energy (keV)	He	N	Ne	Ar	Kr	Xe
2	887	1.6	0.9	1.1	0.06	0.08
3	3589	5.4	2.7	3.3	0.1	0.2
5	21459	26.1	12.2	1.3	0.8	0.3
8	$114 \times 10^3$	117	50.9	4.7	2.8	0.6
10	$250 \times 10^3$	241	102	8.8	5.2	1.0
15	etc	910	366	29	2.3	3.0
20		2356	916	70	4.9	6.8
Absorption edge(s) (eV)	24.6	401.6	866.9	3202.9	14325.6	34561.4
					L <sub>I</sub> 1921.0	5452.8
					L <sub>II</sub> 1727.2	5103.7
					L <sub>III</sub> 1674.9	4782.2

$I_F$  is proportional to  $I_0$ , and is due to scattered radiation of the desired energy. The onset of S K-fluorescence excited by harmonics creates the steep rise in the curve and was found to be a sensitive indicator of beam harmonics. This technique of detuning can be done very quickly without additional energy sensitive detectors and also may be easily and frequently checked.

### 3. Absorption edge data

Here we illustrate a variety of absorption edge data for S, Cl, Ar, and K in order to illustrate the performance of the spectrometer and to show that the sensitivity of detection and the resolution is sufficient for quality work. With the exception of the KCl (focused data) in fig. 6, all data were obtained on beam line VII-3. The S K-edge data in fig. 4 illustrates the sensitivity of the X-ray absorption near edge structure (XANES) to the bonding environment of S in various organic compounds. The zero of energy was chosen as the first inflection point for elemental S. Each compound is identified on the graph. The data show a remarkable sensitivity to the chemical environment of S. In fig. 5 data from S in Illinois No. 6 Coal (1.2 wt.% S) and possibly related reference compounds are shown. Since

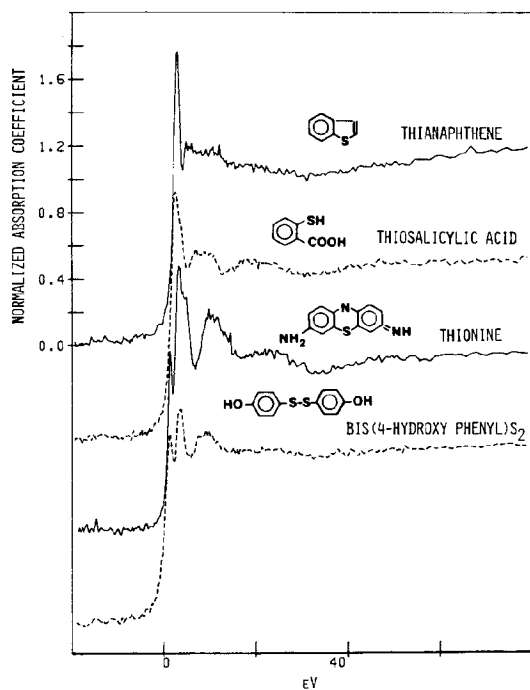


Fig. 4. S K-edge spectra for a variety of organic sulphur compounds. The zero of energy is taken at the first inflection point of pure S at 2472 eV.

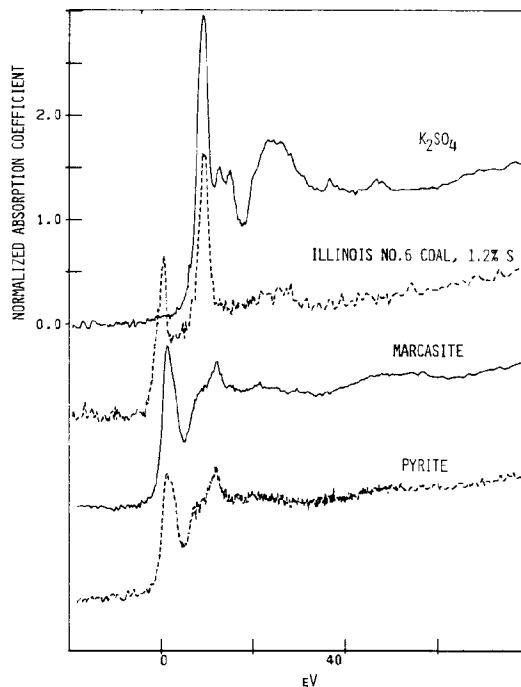


Fig. 5. S K-edge spectra for some inorganic sulphur compounds and a coal.

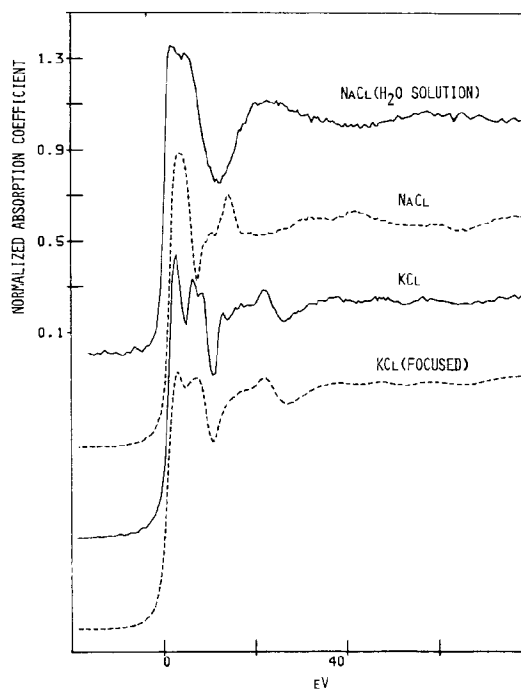


Fig. 6. K-edge spectra for chlorine in the indicated compounds. The lower curve was obtained on beam line II-3 in focusing mode and shows a large degradation of resolution.

our data base of S reference compounds was small our identification must be tentative; however, a significant fraction of the S in Illinois No. 6 appears to be in a mixture of sulfate and pyrite (or marcasite) environments. For comparison, in Hussain et al. [2] the spectrum for subbituminous coal (fig. 8) is very similar to our Illinois No. 6 coal. We have also recently identified a Winifrede seam coal as containing thianaphthene and pyrite-like S [9].

On the basis of comparing the sulfate-like peak at  $\sim 10$  eV our resolution appears to be significantly better than JUMBO (2 eV versus 3 eV fwhm) as it should be considering that a focusing mirror and Ge(111) crystals were used on JUMBO. The sharp little spikes appearing on the curves in figs. 4 and 5 are diffraction peaks from the polycrystalline powder samples which enter the detector. In general, they could be minimized by grinding to a finer texture or eliminated with a suitable filter.

In fig. 6 a variety of Cl K-edge data are compared. In the top two curves a  $\sim 1$  M NaCl-in- $H_2O$  solution is compared with polycrystalline NaCl. In the bottom two curves data for polycrystalline KCl is compared from the wiggler side station, line VII-3, and from the focused line, II-3. Note the serious degradation in resolution on the focused line although Si(111) crystals were used with each monochromator. This is due to the mixing of horizontal and vertical divergence by the focusing mirror. The high resolution KCl data is nearly an exact copy of that of Parratt and Jossem [5]. Also note that the same observation applies to the K K-edge data for KCl in fig. 8. It is remarkable that the Cl XANES out to 20 eV is so different in such similar compounds electronically and structurally as NaCl and KCl.

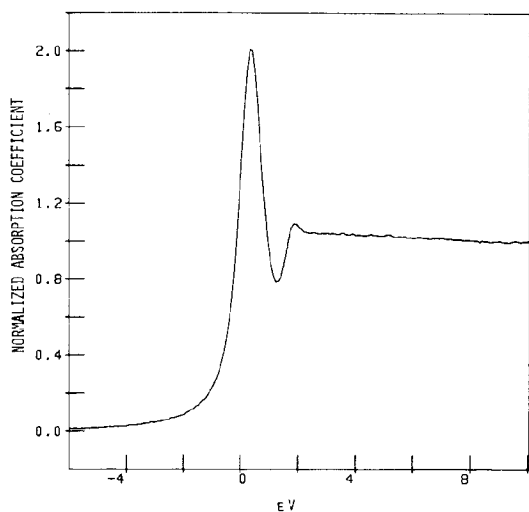


Fig. 7. K-edge spectra for gaseous argon.

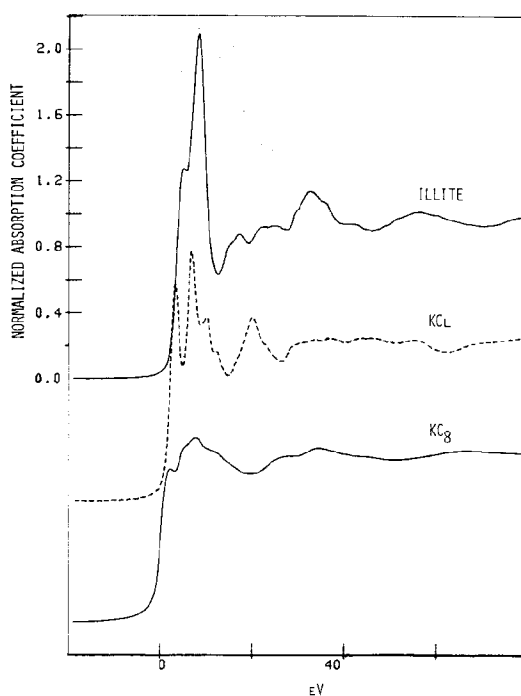


Fig. 8. K-edge spectra for potassium in selected compounds.

The Ar gas K-edge is shown in fig. 7. This spectrum is a classic test of X-ray spectrometry and was first measured at high resolution by Parratt [3] and later remeasured by Schnopper [4]. Both used high resolution monochromators operated in the (1, +1) dispersive mode and equipped with cleaved, polished, and etched calcite crystals. A numerical resolving power,  $\lambda/\Delta\lambda \approx 10000$ , was claimed [5]. The uncorrected fwhm of the first peak was  $\sim 0.8$  eV as compared to  $\sim 1$  eV for the data in fig. 7. The resolution of the spectrometer will be discussed later.

The K K-edge data in fig. 8 illustrate the sensitivity of XANES to three K environments. Illite is a hydrated aluminosilicate mineral having a sheet structure composed of two layers of  $SiO_4$  tetrahedra and one central octahedral  $AlO_6$  layer. K is located between the  $SiO_4$  layers of two adjacent sheets and is 12-coordinated by oxygen. KCl has a cubic structure in which each atom is surrounded by six of the opposite kind. In  $KC_8$  K is intercalated into graphite between two  $C_6$  rings with 12 C first neighbors.

#### 4. Resolution of monochromator

It has been pointed out by Brown [10] and by Kostroun and Materlik [8] that with existing synchro-

Table 2  
Calculated energy band widths for Si(111)

$E$ (eV)	$\delta E$ (eV) <sup>a)</sup>	$\Delta E$ (eV) <sup>b)</sup>	$\Delta E'$ (eV) <sup>c)</sup>	$\Delta E_{\text{total}}$ (eV) <sup>d)</sup>
2472	0.32	0.09	0.8	0.5
3203	0.41	0.20	1.5	0.6
4966	0.65	0.57	3.5	1.
8048	1.14	1.6	7.7	2.

a) Estimated from calculated Si(111) single crystal diffraction profile [11].

b) Assumes constant  $5 \times 10^{-5}$  divergence through 1 mm slit.

c) Assumes full divergent beam from wiggler,  $\text{fwhm} = 2.2\sigma$ ,  $\sigma \approx \gamma^{-1} (E_c/3E_x)^{1/2}$  where  $\gamma^{-1} = 0.170$  mrad.  $E_c = \text{critical energy} \approx 10$  keV and  $E_x$  is the energy of the emitted X-rays.

d)  $\Delta E_{\text{total}}^2 = 2\delta E^2 + \Delta E^2$ .

tron sources the energy resolution is usually determined by the divergence of the emitted X-rays, not by the diffraction width of the monochromator crystals. This was not generally true for our experiments. The 1 mm entrance slit fixed the vertical divergence at  $5 \times 10^{-5}$  rad which was a smaller divergence than that accepted by Si(111) at these low X-ray energies. Various energy band widths are estimated in table 2.  $\delta E$  is the width due to the diffraction profile [11],  $\Delta E$  assumes a constant 1 mm slit and  $\Delta E'$  is the calculated divergence for a wiggler line with electron energy of 3 GeV and wiggler field of 18 kG. The divergence from a SPEAR bending magnet is  $1.2 \times 10^{-4}$  rad [10]. It is obvious that below 5 keV the crystal diffraction pattern dominated the energy band width. At the lowest energies the slit could have been opened to 3 mm for more intensity without degrading the energy resolution.

The resolution of two-crystal monochromators has been discussed [12,13]. The total band pass of the spectrometer is a convolution of the divergence of the source and the width of each diffracting crystal. It also has been demonstrated that measured spectral data may be deconvolved provided that each component of the total resolution is accurately known [14]. Since this is not generally the case a useful estimate of the width of the total instrument function may be made by assuming that every resolution component is Gaussian in shape, hence the components add in quadrature [13].

$$\Delta E_{\text{total}}^2 = \delta E_1^2 + \delta E_2^2 + \Delta E_{\text{source}}^2,$$

where  $\delta E_1$  and  $\delta E_2$  refer to the two crystals, which are identical in this case, and  $\Delta E_{\text{source}}$  is the divergence of the emitted X-ray beam (here limited by a 1 mm slit). This approximation is certainly contrary to what is known about the actual shape of  $\delta E$  and  $\Delta E$  but is used here (as it was in the past) as a rough estimate of  $\Delta E_{\text{total}}$ .

The Ar and KCl data provide a basis for comparison with very well characterized monochromators described in the literature [3,5]. These instruments used calcite crystals with a numerical resolving power  $\lambda/\Delta\lambda \approx 10000$

or an energy band width of  $\Delta E \approx 0.3$  eV at the Ar K-edge. The relative quality of our data and theirs suggests that our estimate of  $\Delta E_{\text{total}}$  is approximately correct as given in table 2.

## 5. Discussion

The feasibility and ease which we have demonstrated here in measuring the K-edge spectra of S under non-vacuum conditions should open up new X-ray spectroscopic investigations of the bonding and structure of S-containing metallo-proteins and other biological materials that are usually vacuum incompatible or unstable. The sensitivity of the fluorescent X-ray detector was a surprise considering that the fluorescent X-ray yield is so low, e.g., 0.07–0.13 for S to K [15]. The explanation lies in the high incident flux and the large solid angle of detection. The qualitative success and relative simplicity of these experiments relative to the severe requirements of a high vacuum environment suggest that new beam lines should be implemented. The excessive thickness of the present Be windows is required not just for a vacuum barrier but also due to the thermal load and possible erosive chemical reactions induced by the X-ray beam. Simply placing the equivalent of the existing monochromator in the vacuum with a thin Be window in the monochromatized beam would result in the spectrum shown in fig. 1a. X-ray intensity equivalent to that now realized for S would extend to the Al K-edge at 1.56 keV. The flux at the S K-edge would be  $10^2$  higher. The end station could be a simple He-filled box with easy access for samples. Si(111) crystals would allow examination of the P K-edge. Some other crystals such as InSb(111) [2] and YB<sub>66</sub>(400) [16] would be required for Si and Al. This suggested beam line would bring a new degree of experimental ease to these frequently occurring elements.

The research of Lytle and Greegor was supported by NSF grants DMR 8013706 and CHE 8219605, the

research of Sandstrom and Marques by NSF grant CHE 8219605 and by ONR. We are all indebted to SSRL for beam time and help from the excellent staff. We particularly thank Dr. G. Brown for a critical reading of the manuscript and Dr. Z. Rek for her calculation of Si(111) Darwin widths [11]. SSRL is supported by DOE, NSF and NIH.

## References

- [1] E. Stern and S. Heald, *Rev. Sci. Instr.* 50 (1979) 1579. Detector obtained from The EXAFS Co., 10815 24th S., Seattle, Washington 98168, USA.
- [2] Z. Hussain, E. Umbach, D. Shirley, J. Stohr and J. Feldhaus, *Nucl. Instr. and Meth.* 195 (1982) 115.
- [3] L.G. Parratt, *Phys. Rev.* 56 (1939) 295.
- [4] H.W. Schnopper, *Phys. Rev.* 131 (1963) 2558.
- [5] L.G. Parratt and E.L. Jossem, *Phys. Rev.* 97 (1955) 916.
- [6] D.R. Sandstrom, SSRL Activity Report (1983) p. VII-109; D.R. Sandstrom and E.C. Marques, *J. Chem. Phys.*, to be submitted.
- [7] Product of Chemplex Industries, Inc., Trademark, X-ray Polypropylene Film.
- [8] Discussions of harmonic rejection by detuning may be found in, e.g., U. Bonse, G. Materlik and W. Schroder, *Appl. Cryst.* 9 (1976) 223; V.O. Kostroun and G. Materlik, *Nucl. Instr. and Meth.* 172 (1980) 215.
- [9] C.L. Spiro, J. Wong, F.W. Lytle, R.B. Gregor, D.H. Maylotte and S.H. Lamsom, *Science*, to be published.
- [10] G. Brown, in *Synchrotron radiation research*, eds., H. Winick and S. Doniach (Plenum, New York, 1980) p. 373. We also thank G. Brown for discussions of the divergence of X-rays from the wiggler beam lines.
- [11] We thank Z. Rek, SSRL, for calculations of the Si(111) Darwin widths in table 2. At 8.05, 4.97, 3.20 and 2.47 keV the fwhm are 7.52, 11.6, 21.1 and 35.8 seconds of arc, respectively.
- [12] A.H. Compton and S.K. Allison, *X-rays in theory and experiment* (D. Van Nostrand, New York, 1935) p. 718.
- [13] A.E. Sandstrom, *Handbuch der Physik* 30 (1957) 151.
- [14] J.O. Porteus, *J. Appl. Phys.* 33 (1962) 700.
- [15] V.O. Kostroun, M.H. Chen and B. Crasemann, *Phys. Rev. A3* (1971) 533.
- [16] J. Wong, W.L. Roth, B.W. Batterman, L.E. Berman, D.M. Pease, S. Heald and T. Barbee, *Nucl. Instr. and Meth.* 195 (1982) 133.